

Effect of HPAM on Calcium Carbonate Crystallization

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ABSTRACT. With the wide application of ASP (alkaline–surfactant–polymer) flooding, the scaling becomes more and more serious, which is harmful to the oilfield and environment. In order to investigate the effects of HPAM on calcium carbonate crystallization, the crystallization behaviors of CaCO₃ in HPAM (Hydrolyzed polyacrylamide) solutions were studied and the composition and morphology of CaCO₃ crystal were investigated in different concentrations of polyacrylamide solutions. The crystal forms and morphologies of CaCO₃ were characterized by Fourier transform infrared spectroscopy, X-ray diffraction and scanning electron microscopy. The results show that the crystallization of CaCO₃ is strongly influenced by the HPAM. The paper analyzed the internal cause, and the results show: The reasons leading to the change of morphology are carboxyl groups in polyacrylamide molecule and Ca²⁺ in solution form chelates by coordination bond. And the chelates are adsorbed on the calcium hydroxide surfaces of solid-liquid interfaces so as to change the formation rate of calcium carbonate crystal nucleus. The research provides a reliable basis for the mechanism research of the scaling problem in the oil extraction process of ASP flooding and the adoption of scale inhibition and scale inhibitor.

Key words: HPAM, Calcium carbonate crystallization, Vaterite, Internal cause

INTRODUCTION

Formation of insoluble mineral salts from supersaturated aqueous electrolyte solution is an important and expensive problem in the several industrial processes such as hydrometallurgy, water desalination, enhanced oil recovery in petroleum industry etc.^{1,2} The mineral scales such as calcium carbonate can deposit at the surface of metals in the heat exchanges, boilers and petroleum production equipment etc. The scale can take place anywhere along the oil pipeline and processing facilities that leads to fouling and increasing turbulences and consequently, blocking the flow line.^{3,4}

Among the barely soluble salts calcium carbonate is one of the most studied. Precipitation of calcium carbonate is a widely occurring process in nature and it is an important industrial product.⁵ Hence its precipitation is of particular interest not only for fundamental research concerning for biomineralization but also their importance in industrial applications.^{6–13} Much of the discussion around scaling has been the formation of scale in the petroleum industry. Calcium carbonate crystallizes in three different anhydrous polymorphs.^{14–16} These are in order of increasing stability; vaterite, aragonite and calcite.^{17,18} Vaterite has a hexagonal structure that usually results in spherulites; aragonite has an orthorhombic structure, often found as needle-like particles, while calcite has a trigonal structure, shaped as

cubes. The least stable polymorph has the highest solubility and will transform by dissolution and re-crystallization into a more stable modification over time.¹⁹ Vaterite and aragonite are thermodynamically unstable and can transform easily to calcite.^{20–24} The initial composition of different polymorphs is determined both by thermodynamics and kinetics.^{25,26}

ASP (alkaline–surfactant–polymer) flooding technology, an important technology of tertiary oil extraction, has been found to enhance oil recovery by over 20%, and it has been used in full-scale in Daqing oilfield which is the most successful case of ASP flooding in the world.²⁷ Therefore, the aim of the present study is to investigate the effect of HPAM (the polymer components in the ASP flooding) on the crystal structure of CaCO₃ deposited.^{28–30} There is few studies have been carried out to study the effect of the HPAM on scale deposition and crystal growth. Thus, understanding the HPAM on crystallization and crystal growth at the surface is important for industrial applications.

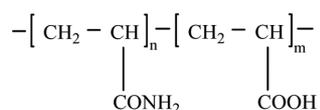
In our experimental system, in order to investigate the effect of the HPAM on the crystal growth polymorphic phases of calcium carbonate, the systematic study of the growth of calcium carbonate in the presence of HPAM was analyzed by XRD and IR. The morphology and the structure of the crystallites were observed by scanning electron microscopy.

EXPERIMENTAL

Materials

The DGG-9023A type of drying oven, electronic balance, constant temperature bath, cyclotron oscillator, Rigaku D/MAX-r type of rotating target X-ray diffractometer (Rigaku Corporation), V33 infrared spectrometer (the company of Germany BRUKER spectrometers), and HITACHI S-3400N type of scanning electron microscope (Hitachi, Japan) were adopted to investigate the effect of HPAM on calcium carbonate crystallization.

The chemical formula of HPAM is:



The anhydrous CaCl_2 , NaHCO_3 , EDTA, KOH, NaOH, and HPAM were adopted in the test, and all of the above agents were analytical pure agents.

Assays for Calcium Ion

This experiment investigates the influence on the concentration of calcium ion under different concentrations of HPAM in 60 centigrade, meanwhile, investigates the remaining concentration of calcium ion under the blank situation using distilled water instead of HPAM.

Test Analysis

The structure and morphology of CaCO_3 were tested and analyzed by X-ray diffractometer and using scanning range of $5\text{--}80^\circ$, V33 infrared spectrometer, and scanning electron microscope.

RESULTS AND DISCUSSION

The Influence of HPAM Concentration on Calcium Carbonate Formation

The results were shown in *Fig. 1* through measuring the concentration of calcium ion in the solution when added different concentration of HPAM. As observed from *Fig. 1*, the remaining concentration of calcium ion firstly increased, and then reduced with the increasing of concentration of HPAM reaches up to maximum at 300 ppm. The *Fig. 1* showed that adding HPAM had a certain inhibitory action to the calcium carbonate scales formation and changed with the concentration changing. Microanalysis also found stable metastable crystal vaterite appeared in calcium carbonate crystal when 300 ppm HPAM added. Obviously, existing in the form of vaterite, Calcium carbonate crystals were

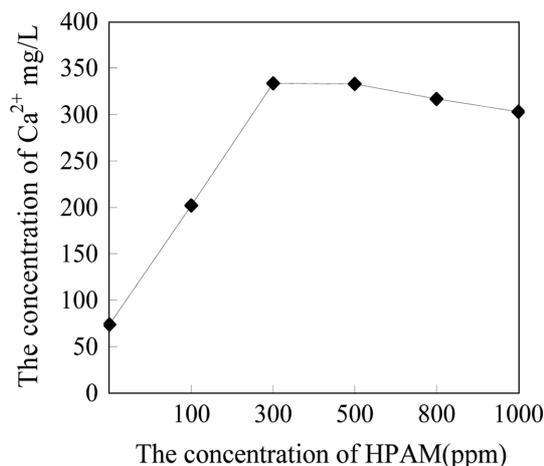


Figure 1. The concentration of calcium ion in the solution with HPAM in different concentration.

not easy to form scales.

The calcium carbonate crystal forms without polyacrylamide and under different conditions of polyacrylamide respectively were analyzed by X-ray diffraction, V33 infrared spectrometer and HITACHI S-3400 scanning electron microscope. In order to ensure the result reliabilities of XRD, IR and SEM, several diagrams with obvious phenomena were selected and analyzed in detail.

XRD Analysis

Fig. 2 to *Fig. 5* are the X-ray diffraction diagrams of calcium carbonate samples under different conditions. Through the analyses of XRD diagrams above, it is indicated that the calcium carbonate crystal exists in the steady state of calcite when no HPAM is added in *Fig. 2*. *Fig. 3* is the XRD diagram of calcium carbonate with 100 ppm HPAM added, and the result shows that a part of calcium carbonate is aragonite crystal form. *Fig. 4* is the XRD dia-

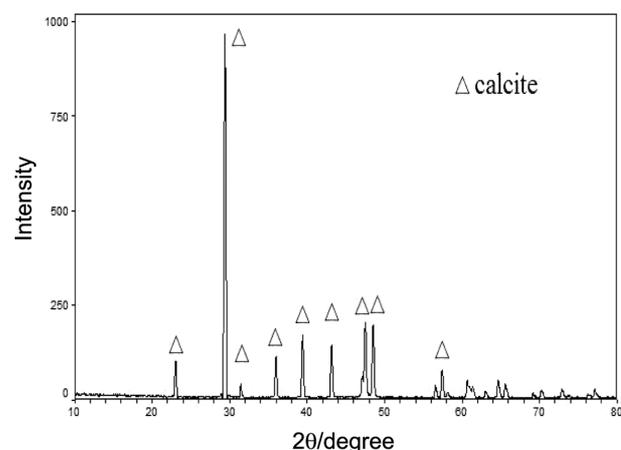


Figure 2. XRD diagram of calcium carbonate without HPAM.

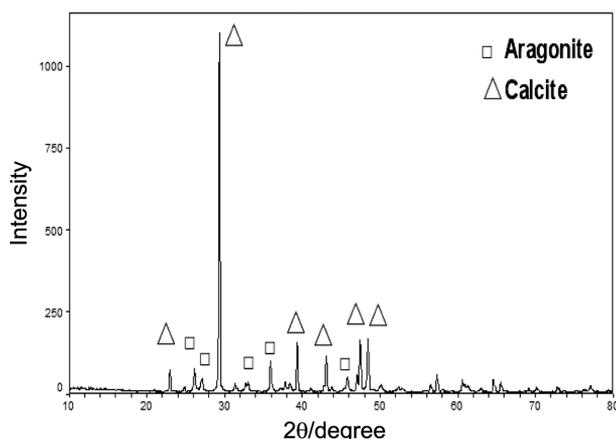


Figure 3. XRD diagram of calcium carbonate with 100 ppm HPAM added.

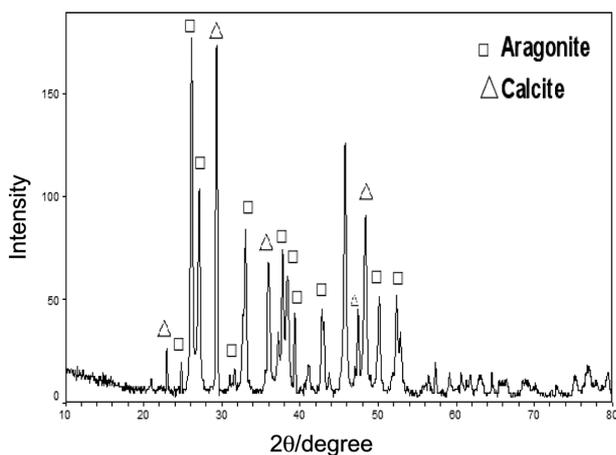


Figure 4. XRD diagram of calcium carbonate with 200 ppm HPAM added.

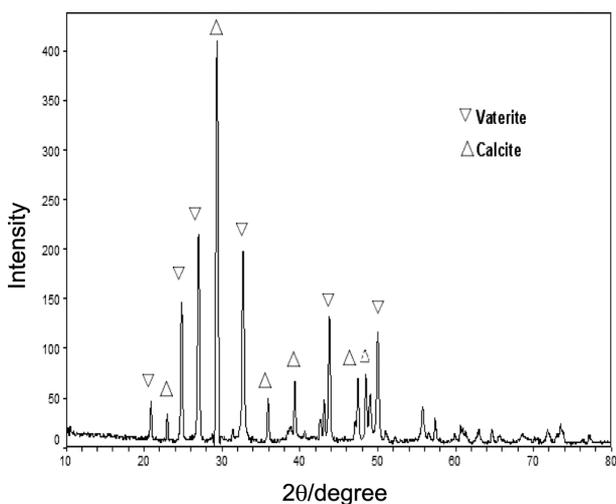


Figure 5. XRD diagram of calcium carbonate with 300 ppm HPAM added.

gram of calcium carbonate with 200 ppm HPAM added. It can be seen that the reaction system polymorphs are mainly aragonite. *Fig. 5* is the XRD diagram of calcium carbonate with 300 ppm HPAM added. It indicated that the polymorphs of calcium carbonate are mainly calcite and the spherical vaterite. It can be known from the analyses of XRD that the addition of HPAM affects the growth and formation of calcium carbonate polymorphs to some extent so that calcium carbonate polymorphs have a tendency to transform to metastable crystal forms.

FI-IR Analysis

The IR spectra lines from down to up in *Fig. 6* are corresponding to the four samples described by *Fig. 2* to *Fig. 5*. It can be seen from *Fig. 6* that the calcium carbonate without HPAM has two absorption peaks respectively at 876 cm^{-1} and 712 cm^{-1} ranging from 900 cm^{-1} to 600 cm^{-1} , and the 712 cm^{-1} is the absorption peak of calcite; however, the IR spectrum of calcium carbonate generated with 100 ppm HPAM added has both the absorption peak of calcite at 712 cm^{-1} and the absorption peak of aragonite at 675 cm^{-1} ; the IR spectrum of calcium carbonate generated with 200 ppm HPAM added has the absorption peak of aragonite at 675 cm^{-1} , and the intensity of this peak is much stronger than that of calcium carbonate peak with HPAM added whose molecular weight is 20 million; the IR spectrum of CaCO_3 generated with 300 ppm HPAM added has the absorption peak of vaterite at 746 cm^{-1} , but its intensity is much lower than that of calcite peak. It indicated that HPAM can cause the change of calcium carbonate polymorphs. It can be known that the HPAM has more inhibition on calcite than on aragonite and vaterite according to the analyses of the results of XRD and IR. It can be also indicated that calcium carbonate is more likely to

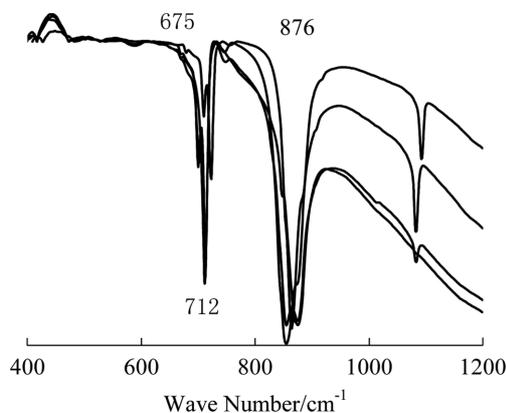


Figure 6. IR spectra diagram of calcium carbonate under different conditions.

exist in the forms of vaterite and aragonite with the presence of HPAM.

Scanning Electron Microscopy

Calcium carbonate crystallizes in the forms of three different anhydrous polymorphs, and their stability is in the order of vaterite < aragonite < calcite. The common morphology of calcite is hexagonal prism or rhombohedron, and often called by cube and fusiform crystal. The shape of aragonite single crystal mainly includes needle-like, leaf-like and massiveness. And the most common form is needle-like crystals. The common shape of vaterite is globular. On the basis of crystal morphologies observed by SEM, the crystal form of calcium carbonate can be determined.

Without HPAM added (*Fig. 7*), calcium carbonate particles exist mainly in form of hexagonal prism, so the crystal of calcium carbonate is mainly calcite. With HPAM added, the morphology of calcium carbonate changes, and deforming hexagonal prism, deforming cube, square piece, spindle shape, rod shape, disc shape, spherical shape, thin slice shape, flower shape and other forms of particles appear. The influence of HPAM on the morphology of calcium carbonate shows the following laws:

(1) Hexagonal columnar crystals become blunt, and the edges of crystals are uneven or the sides of the crystals become uneven (see *Fig. 8* and *Fig. 9*). The morphologies are very similar to the forms of calcite single crystals, when HPAM has a little influence on the morphology of calcium carbonate scale.

(2) With the higher concentration of HPAM added, spherical shape scale appears. Spherical shape scale is clearly shown in *Fig. 10*. The morphology of the above scale has completely changed when compared with that of crystals

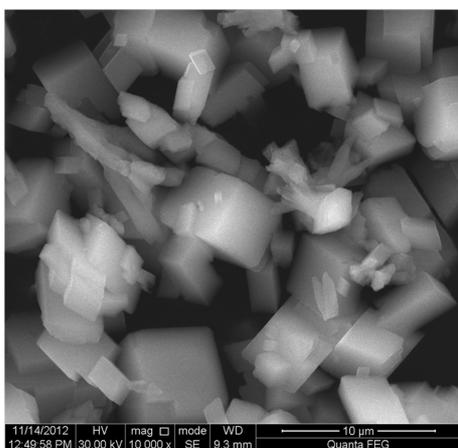


Figure 7. SEM image of calcium carbonate without HPAM.

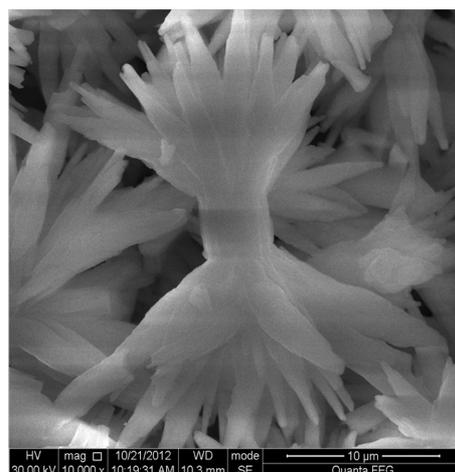


Figure 8. SEM image of calcium carbonate with 100 ppm HPAM added.

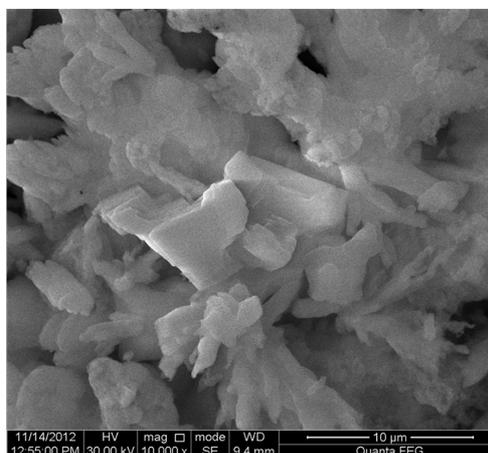


Figure 9. SEM image of calcium carbonate with 200 ppm HPAM added.

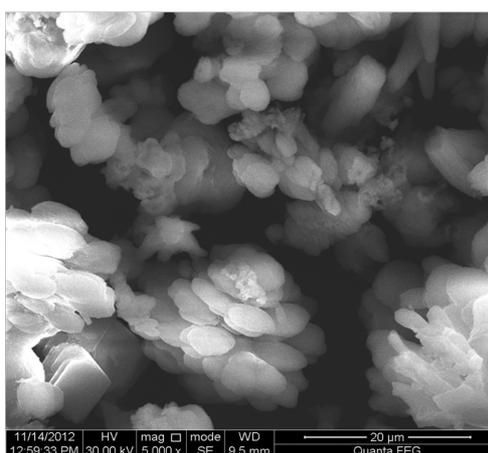


Figure 10. SEM image of calcium carbonate with 300 ppm HPAM added.

without HPAM added, so HPAM has much effect on the growth habit of scale in this condition.

Intrinsic Factor Analysis of Crystal Type Change

It is generally thought that when the organic matter interacts selectively with crystal surface network in some direction by molecular recognition, its growth position will be hindered so that crystal growth rate in the direction perpendicular to this surface in relative to that of other direction surface network will be greatly reduced or even stop growing, thus this surface network is relatively stable and reflected in the final form. Under the action and regulation of HPAM, the spherical CaCO_3 crystal is formed, and its reasons are probably because the stereochemistry conformational change of polymer in the aqueous solution induces a special morphology nucleation and growth of CaCO_3 crystal. The experimental results show that with an increase in the amount of HPAM, calcium carbonate has a growth tendency to convert to globular shape from hexagonal prism. The reasons to lead to the change of morphology may be because carboxyl groups in polyacrylamide molecule and Ca^{2+} in solution form chelates by coordination bond, and then the chelates are adsorbed on the calcium hydroxide surfaces of solid-liquid interfaces so as to change the formation rate of calcium carbonate crystal nucleus.

CONCLUSIONS

(1) HPAM affected the crystallization process of CaCO_3 , so the metastable vaterite type of CaCO_3 crystal was obtained which is difficult to exist in the water. The main morphology of CaCO_3 crystal converts to metastable aragonite and vaterite from steady state calcite.

(2) With the higher concentration of HPAM, it has the greater effect on the crystal form of calcium carbonate. HPAM slows down the transformation from aragonite and vaterite to calcite. HPAM can control the crystallization behaviors of calcium carbonate scale. With the high concentrate of HPAM added, spherical scale is produced.

(3) The reasons to lead to the change of morphology may be because carboxyl groups in polyacrylamide molecule and Ca^{2+} in solution form chelates by coordination bond, and then the chelates are adsorbed on the calcium hydroxide surfaces of solid-liquid interfaces so as to change the formation rate of calcium carbonate crystal nucleus.

(4) The research provides a reliable basis for the mechanism research of the scaling problem in the oil extraction process of ASP flooding and the adoption of scale inhibition and scale inhibitor.

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